Supplementary Information for:

E-H Bond Activations and Hydrosilylation Catalysis with Iron and Cobalt Metalloboranes

Mark A. Nesbit, Daniel L. M. Suess, Jonas C. Peters*

Division of Chemistry and Chemical Engineering, California Institute of Technology, 1200 East California Boulevard, Pasadena, California 91125, United States

Email: jpeters@caltech.edu

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Table S1. XRD experimental parameters for **1a**, **1b**, **1c**, **1d**

Compound	**1a**	**1b**	**1c**	**1d**
Chemical Formula	$C_{36}H_{46}BP_2OFe$	$C_{72}H_{94}B_2P_4S_2Fe$	$C_{43}H_{50}BNP_2Fe$	$C_{39}H_{49}BN_2P_2Fe$
Formula Weight	623.37	1280.87	709.48	674.44
T (K)	100(2)K	100(2)K	100(2)K	100(2)K
λ (Å)	0.71073	0.71073	0.71073	0.71073
Space Group	C_2/c	$P2_1/n$	$P2_1/n$	$P2_1/n$
A	17.9786(7)	11.5444(9)	11.1418(5)	11.9514(10)
B	10.8974(4)	19.5804(15)	12.7713(6)	22.7818(15)
C	33.4789(14)	16.0331(13)	30.2507(13)	13.2520(11)
A	90.00	90.00	90.00	90.00
B	90.6720(11)	110.525(5)	96.033(2)	102.923(5)
Γ	90.00	90.00	90.00	90.00
Volume	6558.7(5)	3394.1(5)	4280.7(3)	3516.8(5)
Z	8	4	4	4
Density (calc)	1.2625	1.2532	1.126	1.272
R1, wr2	0.0412, 0.1001	0.0475, 0.1230	0.0522, 0.1565	0.0537, 0.1729

$R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2\}^{1/2}$

Table S2. XRD experimental parameters for **2**, **2a**, **2b**, **2c, 2-Br**

Compound	**2**	**2a**	**2b**	**2c**	**2-Br**
	$C_{30}H_{463}BN_2P_2Co$	$C_{36}H_{46}BP_2OCo$	$C_{36}H_{46}BP_2SCo$	$C_{43}H_{50}BNP_2Co$	$C_{30}H_{41}BP_2BrCo$
Formula Weight	561.33	626.45	642.51	712.57	613.25
T (K)	100(2)K	100(2)K	100(2)K	100(2)K	100(2)K
λ (Å)	0.71073	1.54178	0.71073	0.71073	.071073
Space Group	P-1	$P2_1/c$	$P2_1/n$	$Pca2_1$	C2/c
A	10.7517(7)	18.2759(14)	10.0753(4)	19.581(2)	18.8235(11)
B	18.0184(12)	8.9584(6)	19.0012(7)	11.1417(13)	9.9502(6)
C	24.6119(15)	21.2277(15)	17.8659(6)	16.9012(12)	31.4070(19)
A	69.741(5)	90.00	90.00	90.00	90.00
B	81.149(4)	107.184(4)	104.7216(16)	90.00	104.505(3)
Γ	74.584(3)	90.00	90.00	90.00	90.00
Volume	4302.0(5)	3320.3(4)	3308.0(2)	3687.2(6)	5695.0(6)
Z	6	4	4	4	8
Density (calc)	1.300	1.252	1.290	1.2835	1.430
R1, wr2	0.0537, 0.1455	0.1088, 0.2698	0.0513, 0.1276	0.0614, 0.1693	0.0293, 0.0658

$R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2\}^{1/2}$

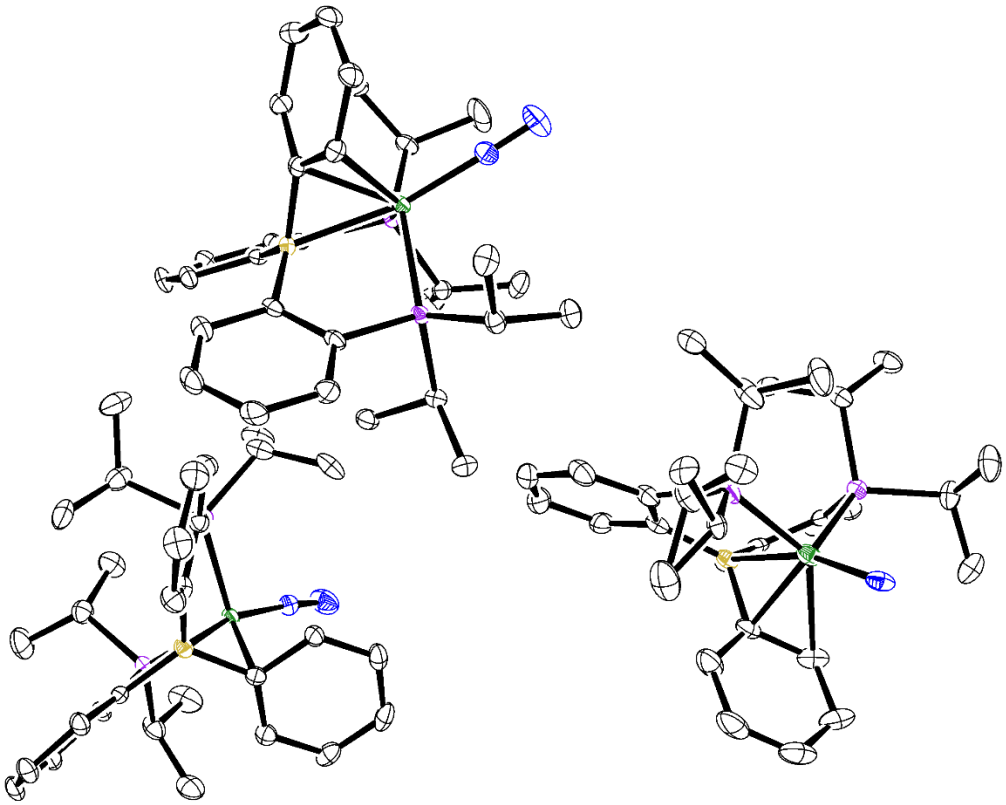

Figure S1. ORTEP representation of the asymmetric unit for **2** (H atoms omitted for clarity). Color Scheme: blue = nitrogen, purple = phosphorus, gold = boron, green = cobalt, black = carbon.

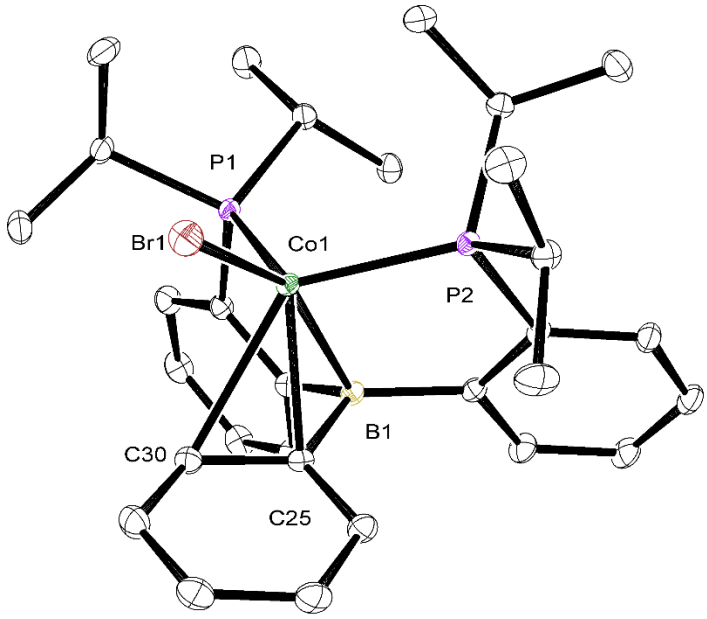

Figure S2. ORTEP Representation of **2-Br** (H atoms omitted for clarity). Selected Bond distances Co1-P1 2.3088(2) Å; Co1-P2 2.2895(2) Å; Co1-C25 2.2485(6) Å; Co1-C30 2.5286(7) Å; Co1-B1 2.3070(7) Å; Co1-Br1 2.36636(16) Å.

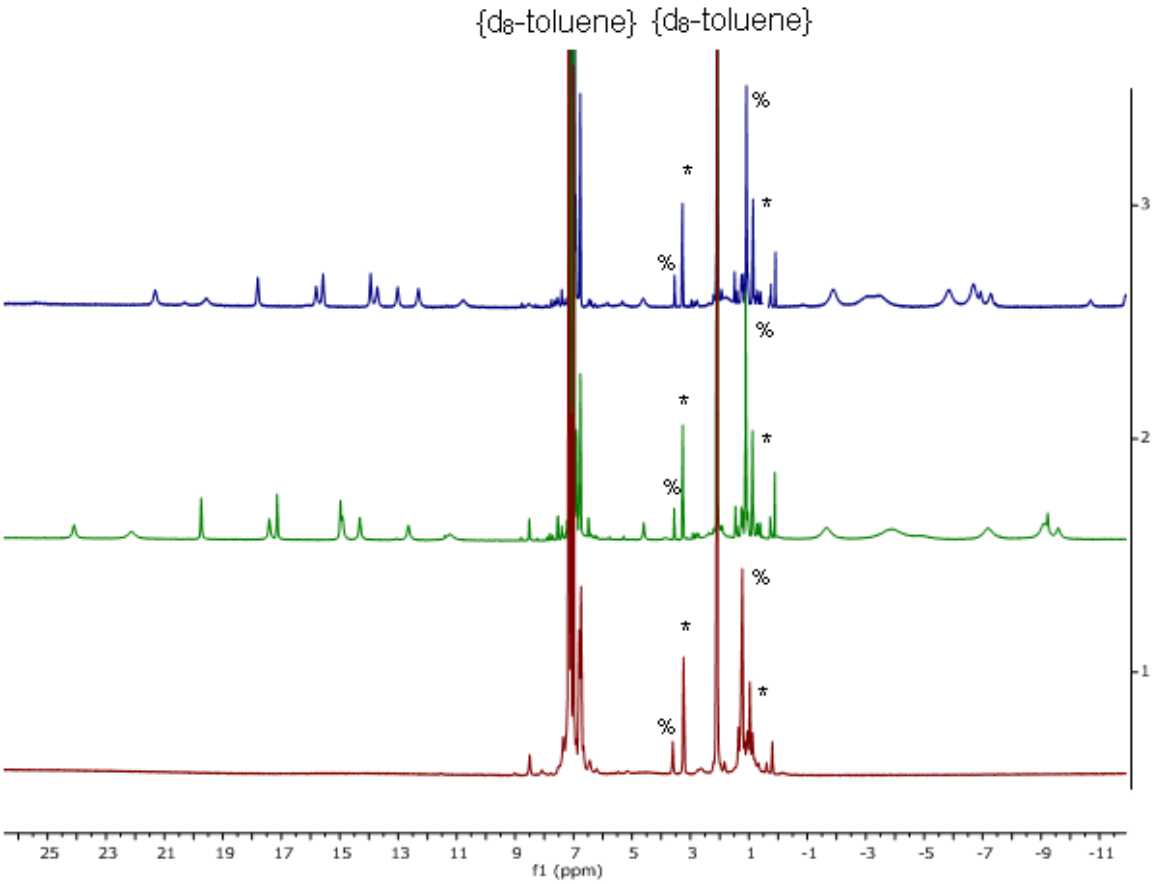

Figure S3. Variable temperature ^{1}H NMR of the reaction mixture of **1d** in d_8-toluene. Red trace is at -90 ^{0}C, green trace is at 25 ^{0}C, blue trace is at 75 ^{0}C. *Et_2O. $^{\%}$THF.

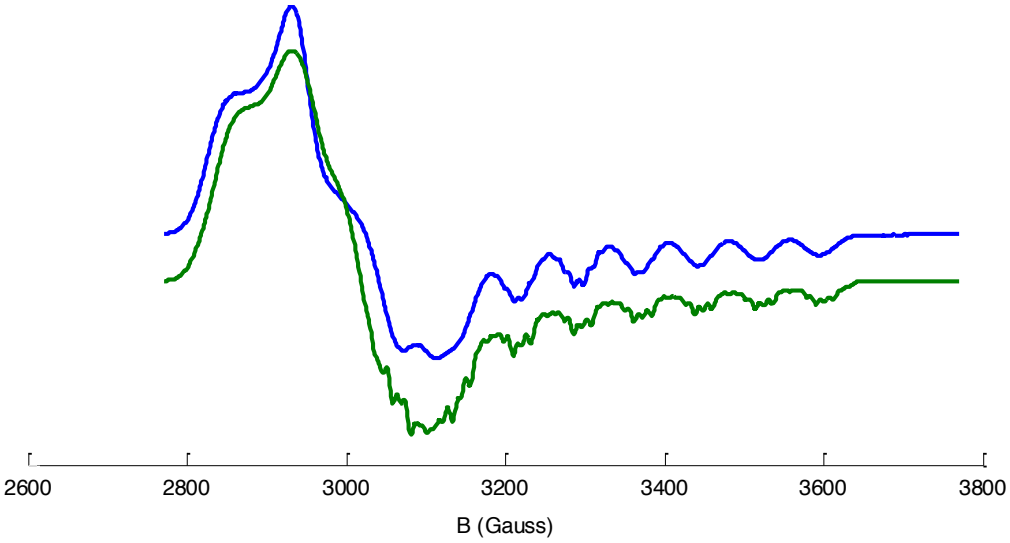

Figure S4. 77 K X-Band EPR spectrum of **2c** in 2-MeTHF (top trace, blue) and simulation (bottom trace, green). Simulation Parameters: g_1: 2.017, g_2: 2.199, g_3: 2.3142. $HStrain_1$: 27.00 MHz, $HStrain_2$: 222.74 MHz, $HStrain_3$: 36.20 MHz. A_{P1} = 63 MHz, 1 MHz, 62.7 MHz; A_{P2}: 63 MHz, 1 MHz, 30.1 MHz; A_H: 30.0 MHz, 1 MHz, 1 MHz; A_N: 30.0 MHz, 160.05 MHz, 141.9 MHz; A_{Co}: 215.1 MHz, 19.7 MHz, 1.0 MHz. Microwave Frequency: 9.398 GHz, Range: 2770 G - 3770 G.

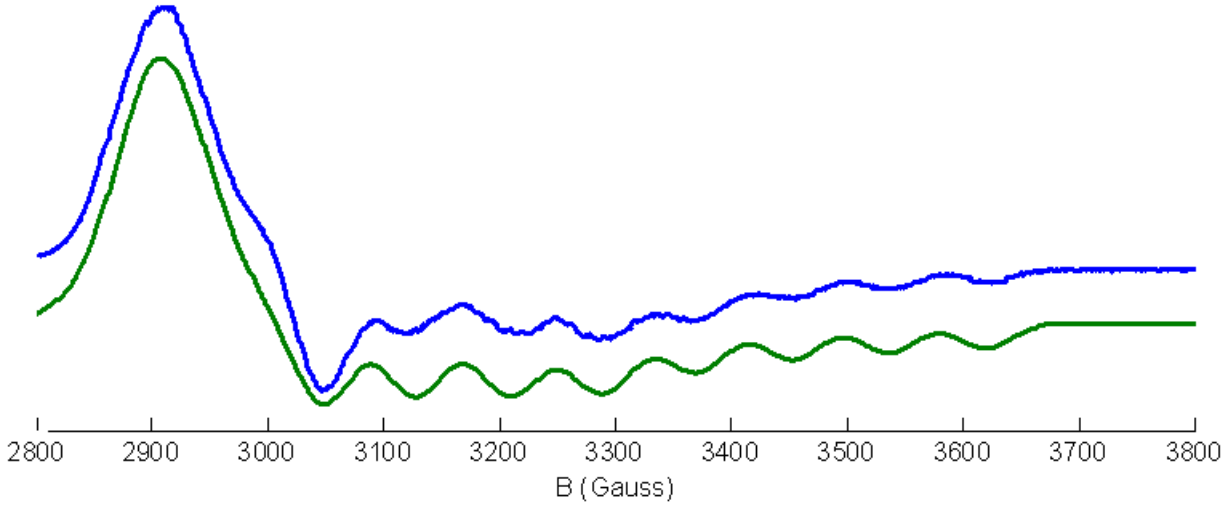

Figure S5. 77 K X-band EPR spectrum of **2d** (top trace, blue) and simulation (bottom trace, green). Simulation Parameters: g_1: 2.0181, g_2: 2.1801, g_3: 2.2679. $HStrain_1$: 142.23 MHz, $HStrain_2$: 384.24 MHz, $HStrain_3$: 226.13 MHz. A_{Co}: 232.51 MHz, 145.42 MHz, 23.80 MHz. Microwave Frequency: 9.412 GHz, Range: 2800 G - 3800 G.

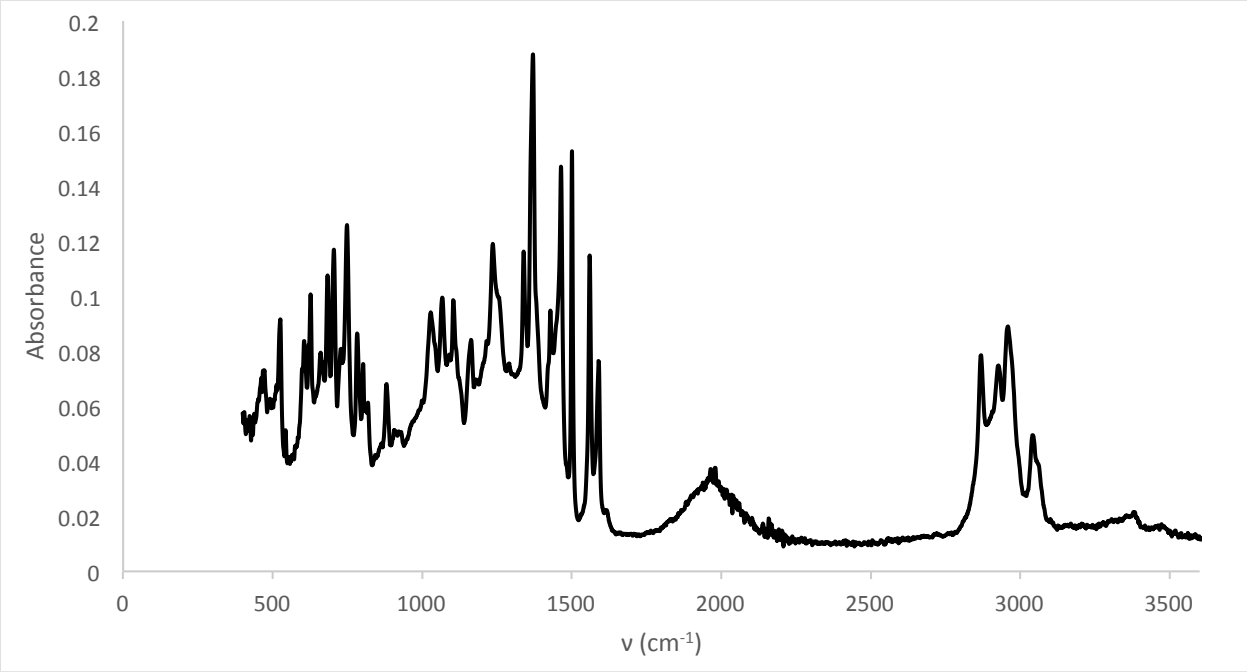

Figure S6. Thin film IR spectrum of **2d** from evaporated C_6D_6.

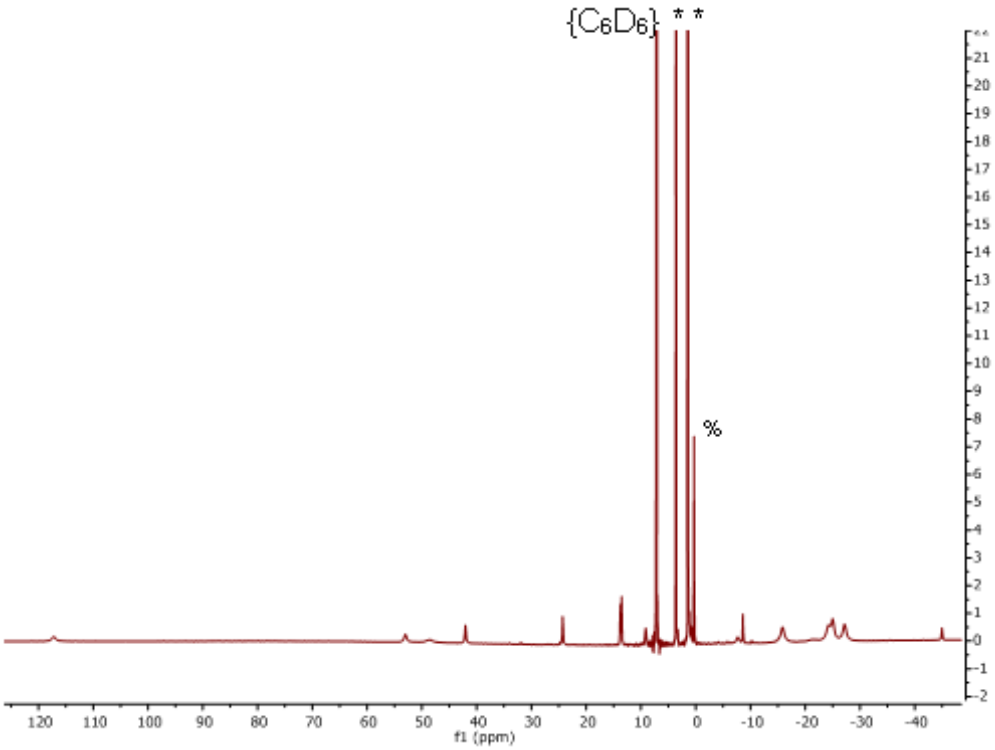

Figure S7. ^{1}H NMR spectrum of **1b** in C_6D_6. *Et_2O. $^{\%}$residual silicone grease.

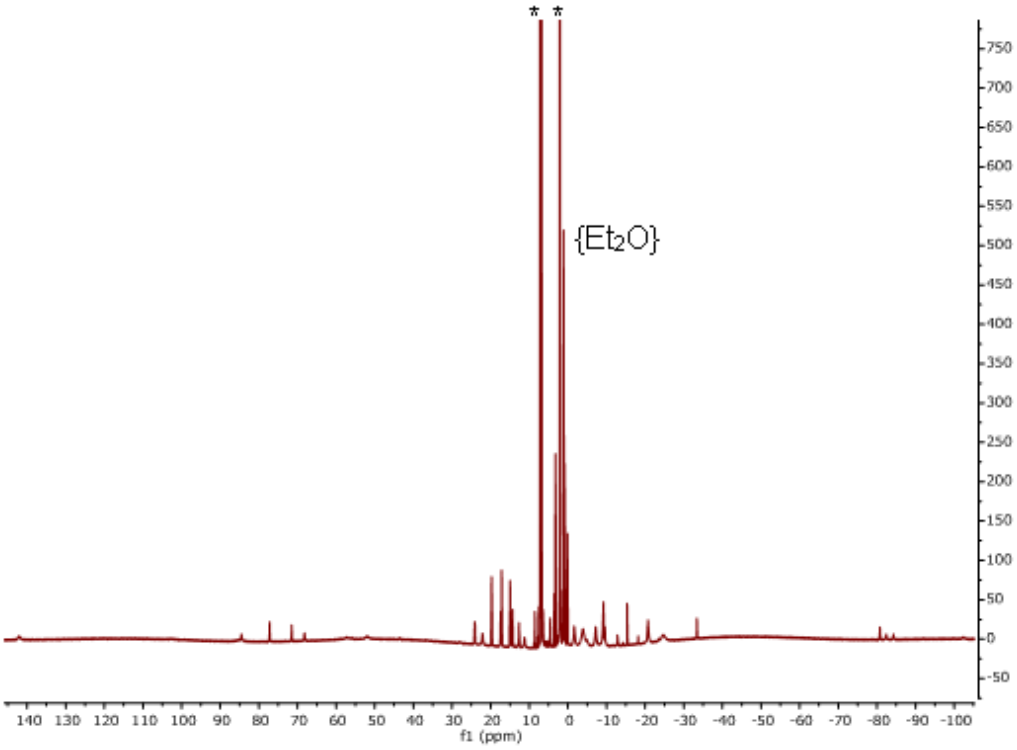

Figure S8. ^{1}H NMR spectrum of **1d** in d_8-toluene (mixture of isomers). *d_8-toluene.

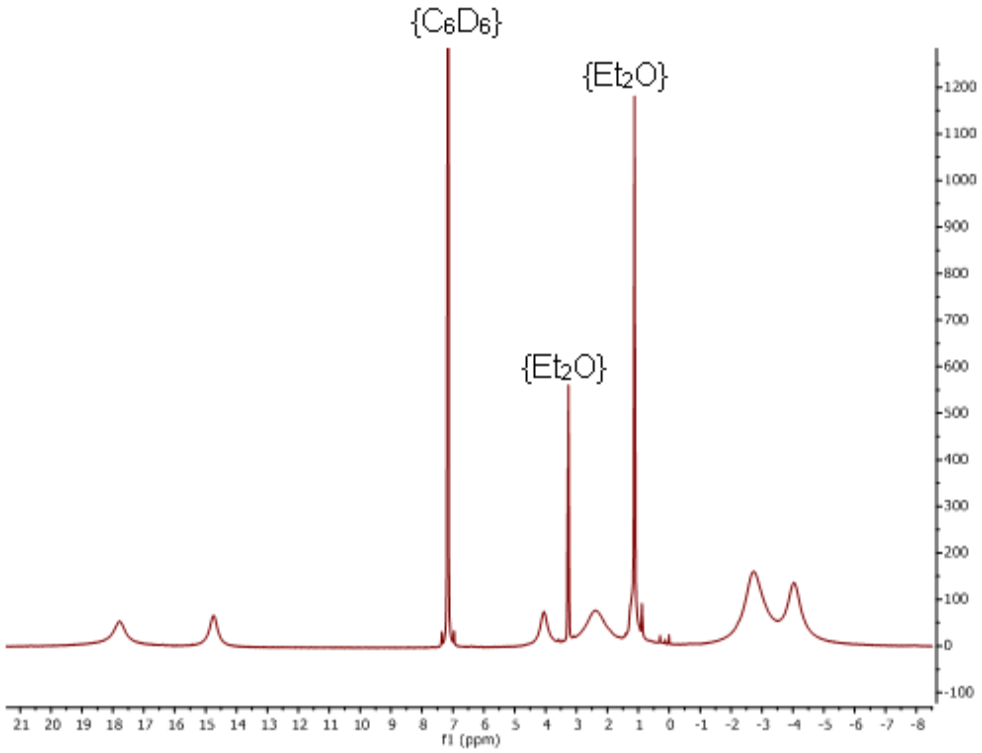

Figure S9. ^{1}H NMR spectrum of **2** in C_6D_6.

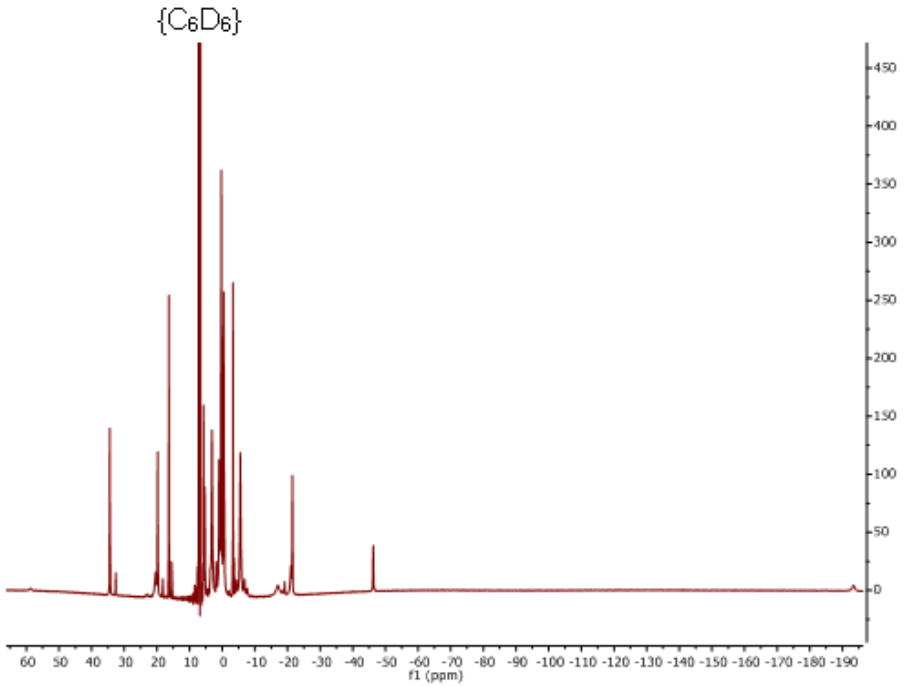

Figure S10. ^{1}H NMR spectrum of **2a** in C_6D_6.

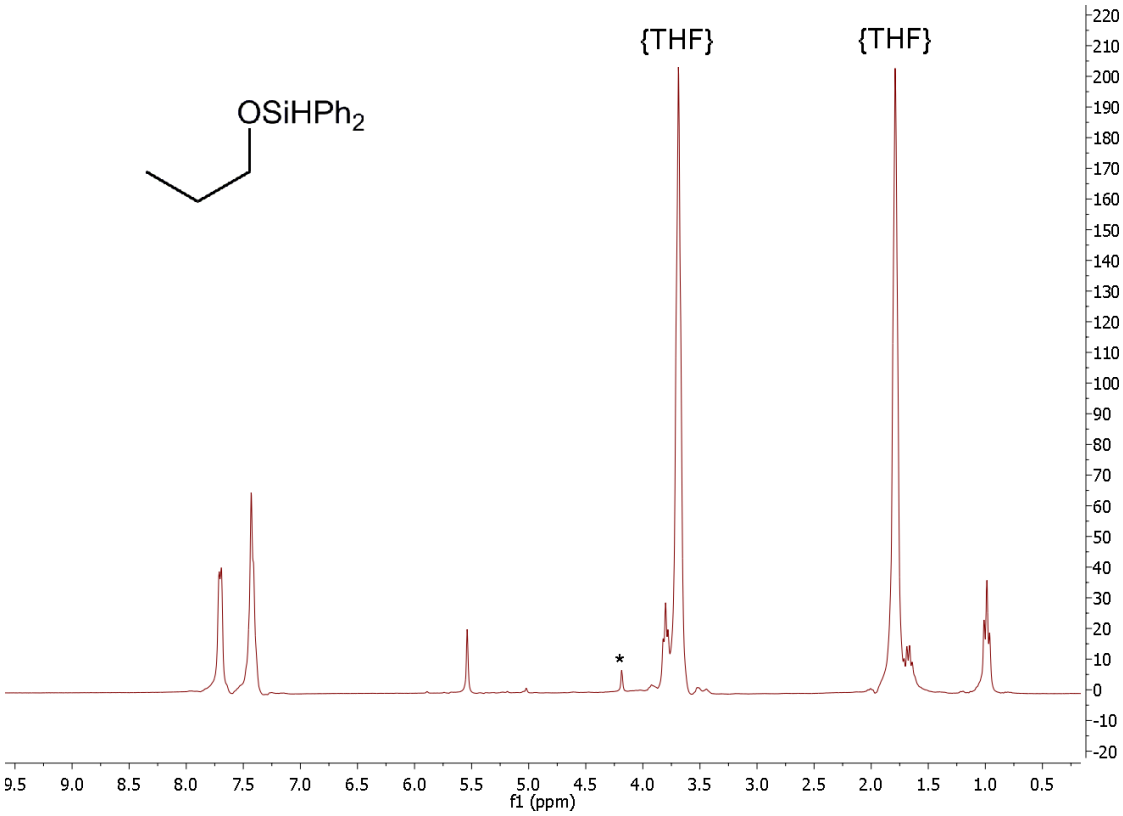

Figure S11. [1]H NMR spectrum of the reaction mixture of Ph_2SiH_2 with propanal in 5:1 THF:d_8-THF catalyzed by **2**. *Ferrocene internal standard.

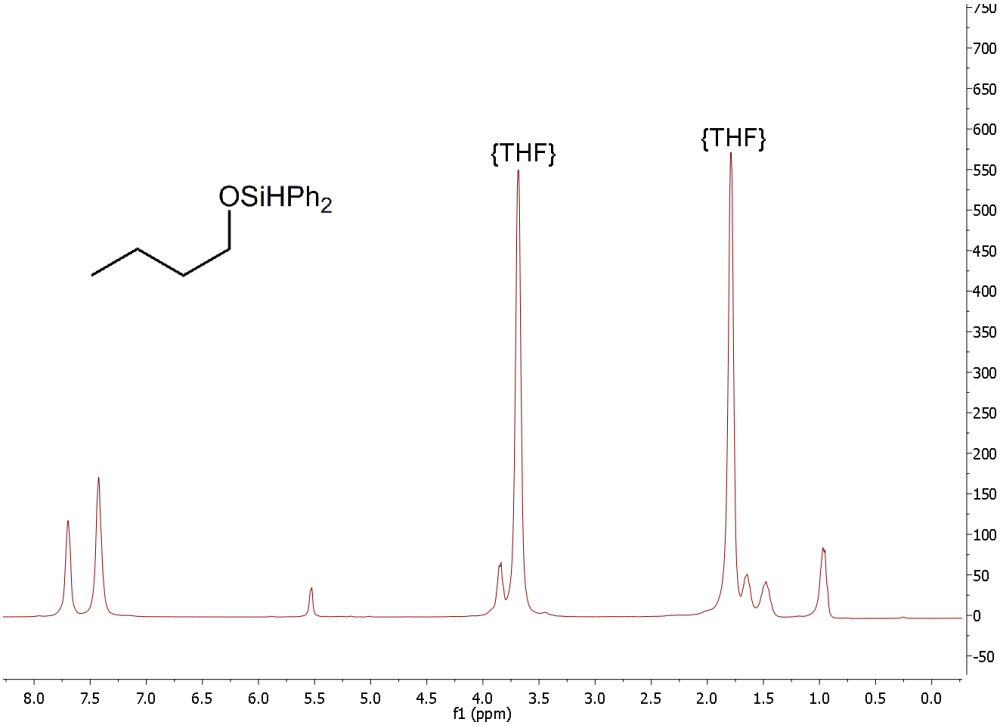

Figure S12. [1]H NMR spectrum of the reaction mixture of Ph_2SiH_2 with butanal in 4:1 THF:d_8-THF catalyzed by **2**.

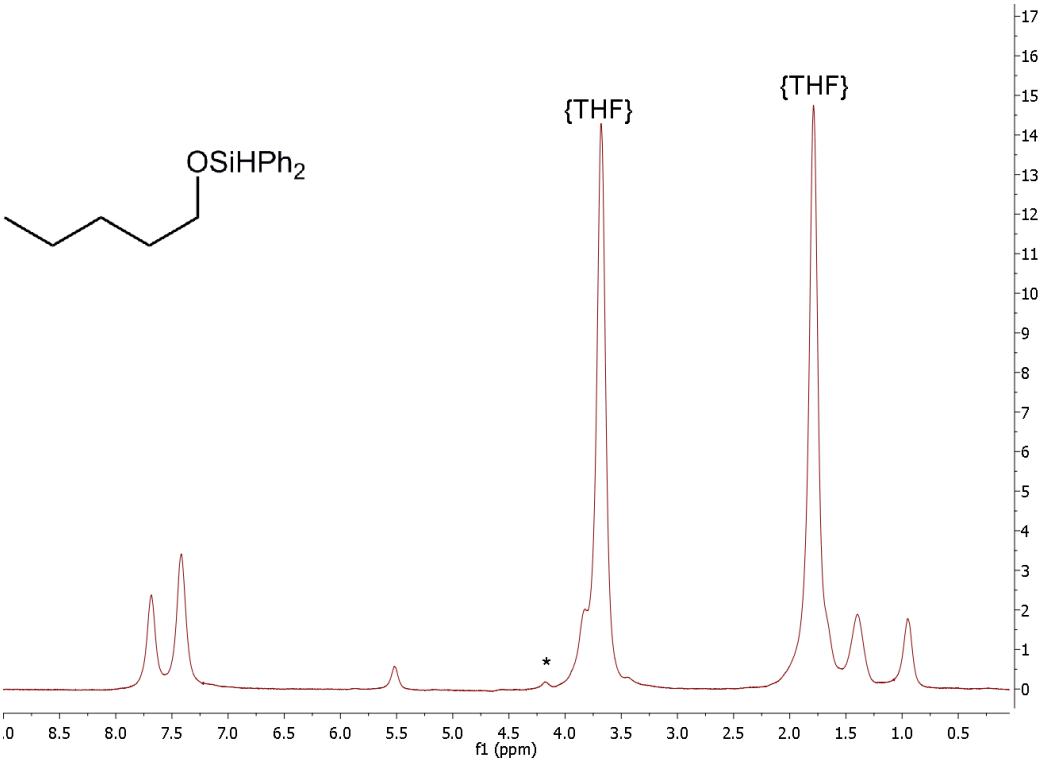

Figure S13. [1]H NMR spectrum of the reaction mixture of Ph_2SiH_2 with pentanal in 4:1 THF:d_8-THF catalyzed by **2**. *Ferrocene internal standard

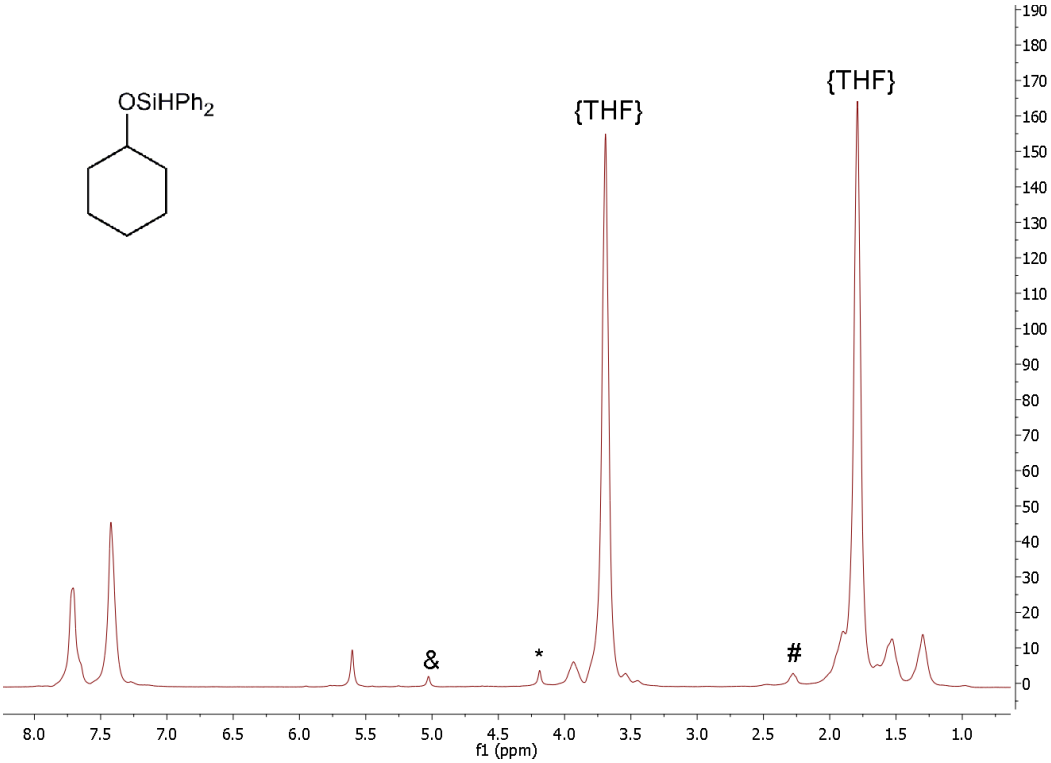

Figure S14. ^{1}H NMR spectrum of the reaction mixture of Ph_2SiH_2 with cyclohexanone in 5:1 THF:d_8-THF catalyzed by **2**. *Ferrocene internal standard. $^{\&}Ph_2SiH_2$. $^{\#}$cyclohexanone.

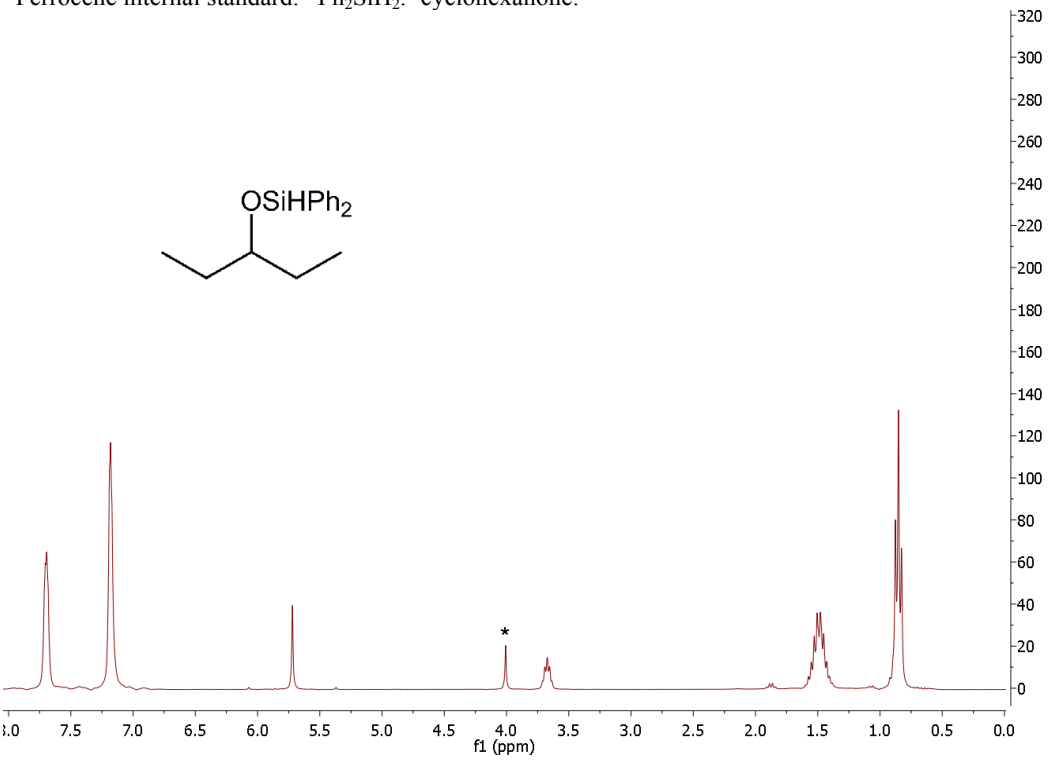

Figure S15. ^{1}H NMR spectrum of the reaction mixture of 2-pentanone with Ph_2SiH_2 in C_6D_6 catalyzed by **2**. *Ferrocene internal standard.

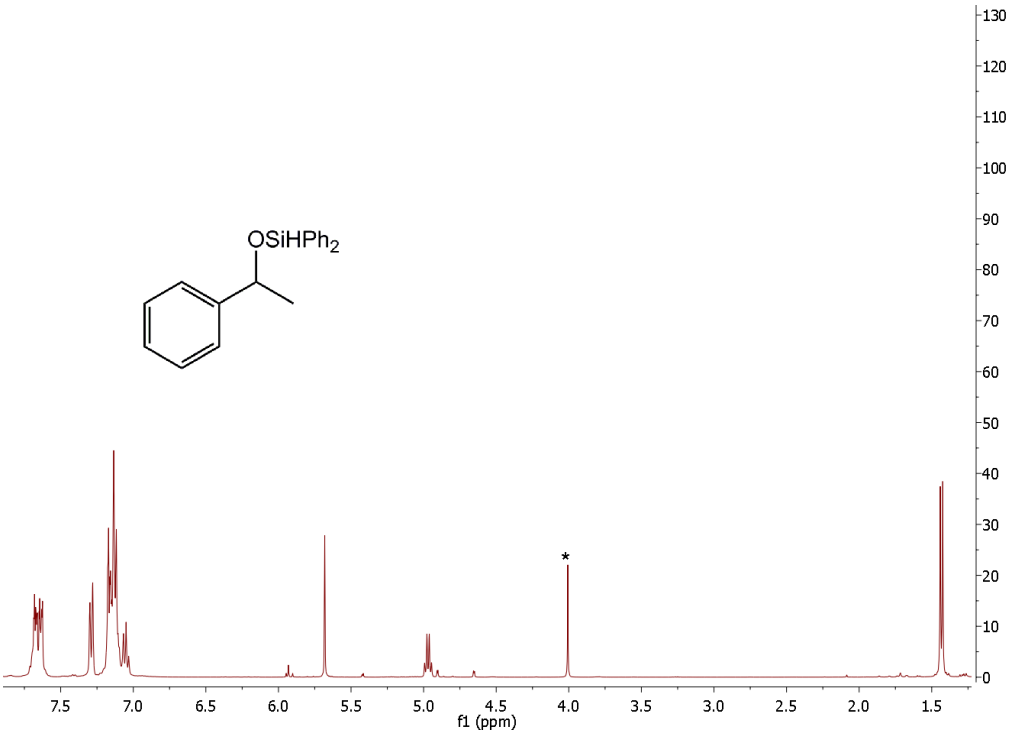

Figure S16. ^{1}H NMR spectrum of the reaction mixture of acetophenone with Ph_2SiH_2 in C_6D_6 catalyzed by **2**. *Ferrocene internal standard.

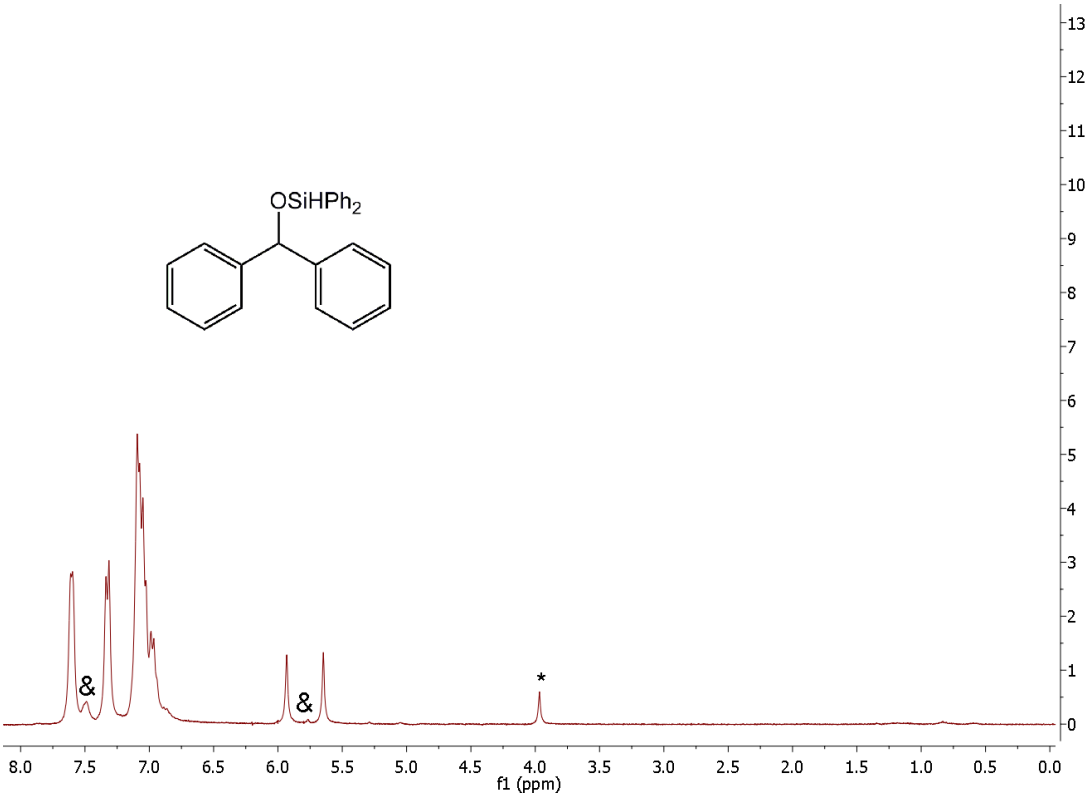

Figure S17. ^{1}H NMR spectrum of the reaction mixture of benzophenone and Ph_2SiH_2 in C_6D_6 catalyzed by **2**. *Ferrocene internal standard. $^{\&}Ph_2SiH_2$.

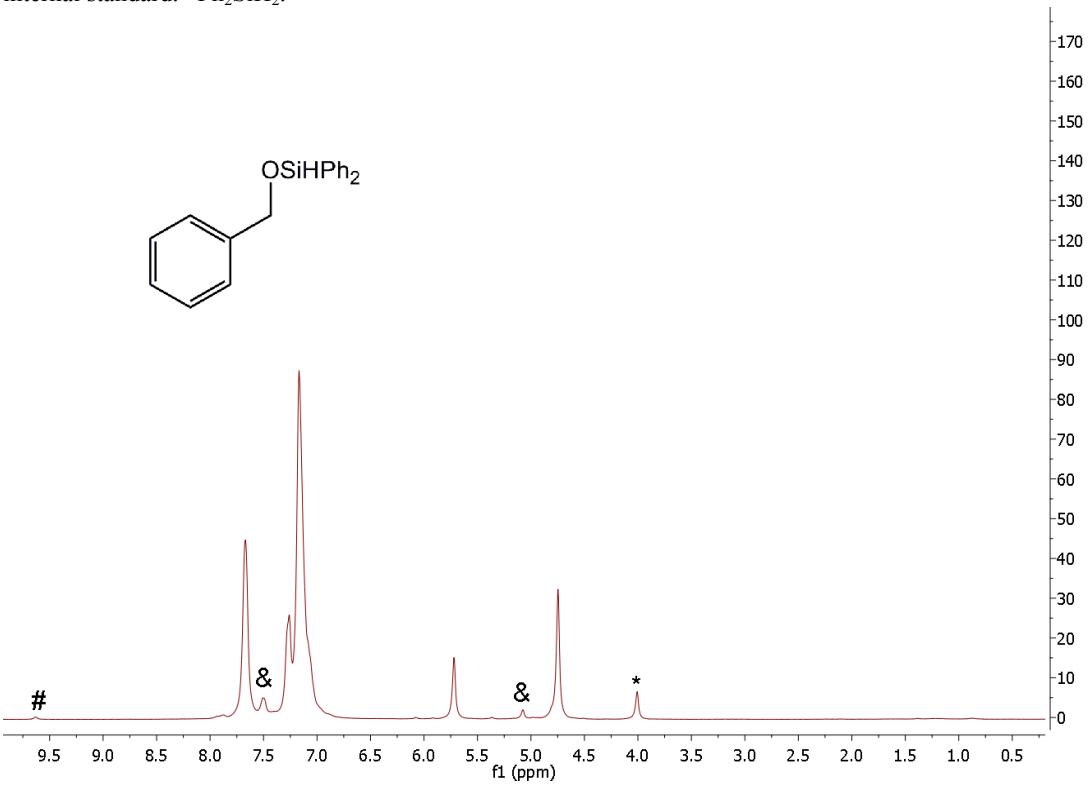

Figure S18. ^{1}H NMR spectrum of the reaction mixture of benzaldehyde and Ph_2SiH_2 in C_6D_6 catalyzed by **2**. * Ferrocene internal standard. $^{\&}Ph_2SiH_2$. $^{\#}$benzaldehyde.